FINGERPRINTING OF WATER CONTAMINATION FROM LANDFILL LEACHATE USING ^{2}H, ^{13}C AND ^{18}O

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by

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LIST OF SYMBOLS AND ABBREVIATIONS

^{2}H / D	Stable hydrogen isotope with mass number of 2/Deuterium	kg/m^3	Kilogram per cubic metre
^{3}H	Radioactive hydrogen isotope with mass number of 3/Tritium	H_2	Hydrogen gas
^{12}C	Stable carbon isotope with mass number of 12	N_2	Nitrogen gas
^{13}C	Stable carbon isotope with mass number of 13	He	Helium gas
^{18}O	Stable oxygen isotope with mass number of 18	CH_4	Methane gas
^{15}N	Stable nitrogen isotope with mass number of 15	mg/L	Milligram per litre
^{34}S	Stable sulphur isotope with mass number of 34	μS/cm	Microsiemens per centimetre
δ	Delta	Cl^-	Chloride ion
EC	Electrical conductivity	SO_4^{2-}	Sulphate ion
‰	Per mill	NO_3^-	Nitrate ion
HNO_3	Nitric acid	HCO_3^-	Bicarbonate ion
NaOH	Sodium hydroxide	Mg^{2+}	Magnesium ion
$BaCO_3$	Barium carbonate	Ca^{2+}	Calcium ion
$BaCl_2$	Barium chloride	K^+	Potassium ion
HCL	Hydrochloric acid	Na^+	Sodium ion
CO_2	Carbon dioxide	m.b.g.l	Metre below ground level
N	Normality	m.m.s.l	Metre mean sea level
Na_2CO_3	Sodium carbonate	H_2CO_3	Carbonic acid
g	gram	CO_3^{2-}	Carbonate ion

LIST OF ACRONYMS

DIC	Dissolved Inorganic Carbon
IRMS	Isotope Ratio Mass Spectrometer
CF	Continuous Flow
EA	Elemental Analyzer
SMOW	Standard Mean Ocean Water
VPDB	Vienna Pee Dee Belemnite
MTW	MINT Tap Water
HDPE	High Density Polyethylene
IC	Ion Chromatography
USEPA	United States Environmental Protection Agency
WES	Water Equilibration System
GC	Gas Chromatography
LC	Liquid Chromatography
VSMOW	Vienna Standard Mean Ocean Water
PDB	Pee Dee Belemnite
MWL	Meteoric Water Line
MMWL	Malaysia Meteoric Water Line
LMWL	Local Meteoric Water Line
IAEA	International Atomic Energy Agency

LIST OF APPENDICES

PENCIRIAN CAP JARI PENCEMARAN AIR DARI AIR LARUTRESAP TAPAK KAMBUS TANAH MENGGUNAKAN ^{2}H, ^{13}C DAN ^{18}O

ABSTRAK

Kajian ini membentangkan tentang penggunaan isotop stabil (^{2}H, ^{18}O dan ^{13}C) bagi penentuan $\delta^{2}H–H_2O$, $\delta^{18}O–H_2O$ dan $\delta^{13}C$–Karbon Inorganik Terlarut sebagai satu kaedah untuk menyiasat pencemaran air larutresap ke dalam takungan-takungan air. Teknik ini melibatkan pengumpulan sampel-sampel air dari tapak kambus tanah di Perak, Malaysia. Kajian ini dijadualkan untuk satu tahun dengan persampelan setiap dua bulan bermula dari bulan Julai 2009 sehingga Jun 2010. Sejumlah 38 sampel air telah diambil dari pelbagai lokasi di kawasan tapak kambus tanah. Sampel–sampel air ini telah disampel dari air permukaan (hulu dan hilir sungai yang terletak berhampiran tapak kambus tanah, kolam dan air larutresap) dan air tanah (telaga-telaga pemantauan). Parameter-parameter fizikal (pH dan konduktiviti) dan ion-ion utama juga telah diukur. Keputusan-keputusan hidrokimia ini adalah sangat penting kerana ianya akan digunakan bersama dengan data-data isotop. Rajah Piper yang diplot menunjukkan perbezaan yang jelas untuk air permukaan (P1) dan air tanah (TP6) dan sampel-sampel air ini menunjukkan evolusi terhasil disebabkan oleh percampuran dengan air larutresap. Sementara itu, TP9 (air tanah) menunjukkan ciri air masin yang sangat jelas. Keputusan-keputusan untuk $\delta^{2}H–H_2O$, $\delta^{18}O–H_2O$ dan $\delta^{13}C$–Karbon Inorganik Terlarut masing-masing berjulat dari +7.70‰ hingga –48.57‰, –0.05‰ hingga –7.56‰ dan +10.60‰ hingga –23.17‰ dengan tanda isotopik yang jelas unik untuk air larutresap, air permukaan (P1) dan air tanah (TP6). Walau bagaimanapun, sungai tidak menunjukkan kesan pengaruh air larutresap dengan tiada tanda isotopik

signifikan. Ini mungkin disebabkan pergerakan air larutresap secara setempat dan terkekang di dalam air tanah atau disebabkan oleh kerana pencairan berlebihan air larutresap di dalam sungai. Pengukuran semua sampel–sampel air untuk nilai–nilai isotop menunjukkan kebolehan teknik nisbah isotop dan boleh digunakan sebagai kaedah yang berpotensi di dalam menentukan pencemaran air larutresap dari tapak kambus tanah. Pencemaran air oleh air larutresap boleh dibezakan dengan nilai–nilai isotop yang lebih positif atau diperkaya.

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ABSTRACT

This study presents the use of stable isotopes (^{2}H, ^{18}O and ^{13}C) for the determination of $\delta^{2}H–H_2O$, $\delta^{18}O–H_2O$ and $\delta^{13}C$–Dissolved Inorganic Carbon ($\delta^{13}C$–DIC) as a method to investigate leachate contamination in water bodies. The technique involves the collection of water samples from a municipal solid waste landfill in Perak, Malaysia. Water sampling was conducted bi-monthly for one year starting from July 2009 to June 2010. A total of 38 water samples were collected from various locations in the vicinity of the landfill. These water samples were taken from surface waters (upstream and downstream of the river, located adjacent to the landfill site, pond and leachate) and groundwater (monitoring wells). The physical parameters (pH and conductivity) and its major ions were also measured. These hydrochemical results are imperative, as it will be used in conjunction with the isotopic data. The Piper diagram plotted showed a variation for surface water (P1) and groundwater (TP6), and these water samples indicated an evolution resulting from mixing with leachates. Meanwhile, TP9 (groundwater) demonstrated a very distinct characteristic of saline water. Results for the $\delta^{2}H–H_2O$, $\delta^{18}O–H_2O$ and $\delta^{13}C$–DIC ranged from +7.70‰ to –48.57‰, –0.05‰ to –7.56‰ and +10.60‰ to –23.17‰ respectively, with unique distinct isotopic signature for leachate, surface water (P1) and groundwater (TP6). However, the rivers showed no sign of leachate influence with no significant isotopic signature. This could very well be due to a very localized and confined leachate movement in the groundwater, or the over dilution of leachate in the river. The

measurements of the water samples for its isotope values corroborated the ability of isotope ratios technique and it can be used as a potential tool in detecting landfill leachate contamination. The leachate-contaminated waters are distinguished by a more positive or enriched isotope values.

CHAPTER 1

INTRODUCTION

1.1 Background

Most South East Asian countries (including Malaysia) are currently facing severe environmental problems, an obvious example being the degradation of surface and groundwater resources (UNESCO, 1996). This degradation is mostly due to impacts of anthropogenic organic and inorganic pollutants, resulting from increase in industrialization, urbanization, and an increase in agricultural activities and population. The sources of these pollutants can be either point or non–point; or both. A point source of surface and groundwater pollution is defined as any single identifiable source of pollution, from which pollutants are discharged, examples being chemicals spills and leakages, industrial and domestic disposal, leachate from a landfills, septic tank effluent and industrial wastewater outfalls, while the source of non–point pollution is more ambiguous, and cannot be referred to any specific point. A major example for this type of pollution is runoff, where pollution from pesticides and fertilizers from agricultural areas during a rainstorm drains itself into major water bodies (Abdul Rahman, 2004).

Groundwater pollution prevention is the primary objective of environmental protection regulations for municipal solid waste landfills. Early detection of groundwater pollution and the determination of its sources are important when considering cleanup or containment programs, as well as legal issues that are

frequently associated with polluted groundwater (EEC, 1993). In a landfill area, due to the presence of multiple sources of anthropogenic pollutants, such as hazardous waste disposal facilities, chemical industries, sewage treatment facilities, agricultural sites, housing and also geogenic factors (seawater intrusions), it could possibly contribute to the groundwater pollution, causing difficulties in differentiating the source of the pollution, thus complicating the interpretation of chemical data from monitoring wells around the landfill (Abdul Rahman, 2004; Libes, 1992).

Currently, 24,000 tonnes of municipal solid wastes are generated in Peninsular Malaysia daily (EPU, 2010). Based on the waste generation trends, this value is expected to increase to more than 30,000 tonnes daily by the year 2020 (Ministry of Housing and Local Government, 2005). There are a total of 301 solid waste disposal sites in Malaysia, however, 111 of these landfills have ceased operations. Out of the 190 still operating, only 5% (10 landfills) can be classified as sanitary landfill (Kementerian Perumahan Dan Kerajaan Tempatan, 2008). There are several cases where landfill leachate leaked into the river that supplies water to the domestic water treatment plant, causing foul–smelling odour in tap water; hence disrupting domestic water supply, and creating health problems. Concerned, the Ministry of Housing and Local Government conducted a study regarding the safe closure and rehabilitation of landfill sites in Malaysia. The conclusion of this study suggested that 16 landfills located near water intake points that pose a significant threat to the well being of the people be closed using safe and acceptable methods (Kementerian Perumahan Dan Kerajaan Tempatan, 2008). The implementation of this policy is however hampered due to the fact that no replacement or alternative sites for solid waste disposal were found, resulting in four of the landfills being allowed to continue operations, with

upgrades to an acceptable level (Level 3 for environment non–sensitive area and Level 4 for environment sensitive area or located near the intake of the water treatment plant for domestic supply) that will ensure minimal damage the environment (Kementerian Perumahan Dan Kerajaan Tempatan, 2008).

At the moment, disposal of solid waste is one of the major environmental problems faced by municipalities in Malaysia. The potential for surface and groundwater contamination from landfills due to landfill leachate was recognized several decades ago especially in developing countries, however, there is still little to no monitoring being undertaken in Malaysia (Ministry of Housing and Local Government, 2006; Mohamed et al, 2009). Moreover, the extent of leachate infiltration, its movement in groundwater, and its discharge to surface water resources is mostly unknown at any recognized waste disposal facilities. Hence, the extent of short and long term contamination of groundwater and surface water resources is presently unknown (Abdul Rahman, 2004).

1.2 Problems Statement

The detection of landfill leachate in surface waters and groundwater adjacent to landfills can be made difficult by limitations of conventionally monitored parameters, which, more often than not, unable to differentiate the different sources of pollution. This research aims to examine the application of stable isotopes in detecting leachate in surface waters and groundwater. It will focus on the use of $\delta^{2}H$, $\delta^{13}C$ and $\delta^{18}O$ measurement of leachate, surface waters and groundwater from rivers adjacent to the

landfill, pond and monitoring wells in order to detect the leachate influence and its level of contamination.

1.3 OBJECTIVES

Three main objectives of this research project are:

a. To measure the isotopic compositions of samples for stable isotopes.
b. To evaluate the relationship of stable isotope values between the water samples and leachate.
c. To synthesis the simplest way to fingerprint surface water and groundwater contamination caused by landfill leachate.

1.4 SCOPE OF WORKS

The scope of this research project will include 2 major elements:

1.4.1 Isotope Hydrology Technique

The major technique used in this research project is the Isotope Hydrology Technique. The IRMS used for isotopic analysis is a specialized mass spectrometer that produces precise and accurate measurements of variations in the natural isotopic abundance of light stable isotopes. If an isotopic signature could be established for a leachate, then the $\delta^{2}H$, $\delta^{13}C$ and $\delta^{18}O$ stable isotope ratios could be used as indicators to identify leachate as contamination sources in a monitored landfill environment.

The IRMS with Continuous Flow Elemental Analyzer mode (CF EA–IRMS) used in this study is faster, simple and requires a smaller quantity of samples for stable isotope analysis for a range of sample types ($\delta^{2}H$–$water_{Liquid}$, $\delta^{18}O$–$water_{Liquid}$ and $\delta^{13}C$–DIC_{Solid}) compared to IRMS with Dual–Inlet mode (DI–IRMS), as stated by Benson et al. (2006).

1.4.2 Hydrogeological and Hydrochemical Techniques

Hydrological and geological conditions are significant parameters being considered in understanding the characteristics and properties of the study area. However, these data are considered secondary, derived from the existing data. The hydrochemical study utilizing conventional technique includes water sampling in order to determine the major ions and measurement of electrical conductivity (EC) and the pH.

1.5 Outline of Thesis

Chapter 1: Introduction

This chapter details the background of the study, its problems statement, the list of objectives and the scope of works.

Chapter 2: Literature Review

This chapter presents the landfill, waste composition, leachate characteristics, leachate movement and its impact to the water bodies. Theories on isotope hydrology and

reviews on stable isotopes application in surface and groundwater studies are greatly elaborated upon in this chapter. Previous works done on surface and groundwater studies using stable isotopes in Malaysia are also explained.

Chapter 3: Materials and Methods

This chapter describes the site used in this study, field sampling techniques, laboratory analyses programs and analytical instruments that were used. The analyses of these water samples are divided into two parts, which are hydrochemical and stable isotopes analysis.

Chapter 4: Results and Discussion

This chapter presents the analytical data obtained from the analyses of the water samples. The unique isotopic characteristics of hydrogen, oxygen and carbon in the leachate, surface waters and groundwater from the study area are also highlighted.

Chapter 5: Summary and Conclusion

This chapter summarises research findings and appropriate conclusion are derived with respect to these findings.

CHAPTER 2

LITERATURE REVIEW

This chapter briefly reviews the fundamentals of isotope hydrology and the use of environmental isotopes (^{2}H or D, ^{18}O and ^{13}C), along with their applications for surface waters and groundwater studies. It will look into the use of environmental isotope analyses of groundwater, surface water and leachate (water, ^{2}H and ^{18}O; and dissolved inorganic carbon, ^{13}C–DIC) as a technique to fingerprint landfill leachate contamination. The typical isotopic composition that is expected from landfill leachate, landfill related surface waters and groundwater, along with the reasons why these waters have such isotopic values characteristic, and how such results can be used as a technique/tool to fingerprint the contamination from a municipal landfill in surface and subsurface environments will also be elaborated. Finally, this chapter presents the previous work conducted on surface and groundwater studies using stable isotopes in Malaysia.

2.1 Landfill

Landfilling is the most economical and environmentally acceptable method for disposal of solid waste (Rodriguez et al., 2004), which is why in Malaysia, it is the most common method used for solid waste disposal (World Bank, 1992; Sakawi, 2011). In general, there are two types of landfills in Malaysia, namely sanitary and unsanitary landfill (open dumping). From a total of 301 disposal sites in Peninsular Malaysia, almost 50% are classified as unsanitary landfill (open dumping) (CAP,

2001). Although landfills are suitable and cost effective waste management method, it is not without its problems. These problems are mainly associated with the operation of the landfills, which are commonly leachate generation, gas production (mostly methane), odours, air pollution, dust, fire hazards, and disease vectors (such as flies and rodents). Another critical problem is the contamination of the groundwater system and the adjacent surface water from the landfill leachate that seeps through the bottom of the unlined landfill or its surface run–off (Miller, 1997).

2.1.1 Solid Waste Composition

At present, the per capita generation of solid waste in Malaysia varies from 0.45 to 1.44kg/day, depending on the economic status of an area. Generally, the per capita generation rate is about 1kg/day. Malaysian solid wastes are highly organic, resulting in high moisture content and a bulk density of above 200kg/m^3 (CAP, 2001). About 70% (vol) of the municipal waste from the urban area in Malaysia is organic, such as putrescible waste and paper, while the rest are plastic and rubber (18%), metal (4.3%), glass and ceramic (4.9%), textile (3.4%) and others (0.9%). Generally, the nature of the waste will determine the pollution parameters in a leachate, with urban wastes resulting in higher pollution parameters in the leachate when compared to suburban or rural waste (Agamuthu, 1999).

2.1.2 Leachate

A leachate is defined as a liquid that has percolated through a solid waste and has successfully extracted dissolved or suspended materials from it. In most landfills, the

liquid portion of the leachate is composed of liquid produced from the waste decomposition with liquid that has entered the landfill from external sources, such as rainfall, surface drainage and groundwater (Peavy et al., 1985).

There are several factors affecting the quantity and quality of a leachate. The leachate quantity is strongly influenced by precipitation, groundwater intrusion, the moisture content of the waste and its final cover. As for final cover, the application of soil will reduce infiltration. Generally, a good design of final cover will help reduce leachate quantity significantly. The factors affecting a leachate's quality are its waste composition, waste depth, availability of moisture and oxygen, landfill design, its operation and its age (Samuding, 2010). Bagchi (1994) stated that a leachate's variation is higher for putrescible waste (for examples: food, paper, textile) compared to non–putrescible waste (for examples: glass, metal, plastic). The concentrations of the pollutants for leachate samples from deeper landfills are higher due to greater time contact between the liquid and the solid phases (McBean et al., 1995). According to Samuding (2010), water and oxygen are the two most important factors in determining waste biodegradability, as it affects the stabilization rate and also determine the type of decomposition, whether aerobic or anaerobic. Normally the leachate's quantity reaches a certain level after approximately two or three years from the time of waste placement. The leachate's peak concentration will gradually decrease, as the quantity of the chemicals in the waste is limited (McBean, 1995).

According to Christensen (1994), there are several groups of contaminants that can be found in leachates from landfill sites such as organic and inorganic matter, and toxic metals (for examples: cadmium, zinc, lead, chromium and copper). The variation of

leachate composition for different landfill sites in Malaysia is shown in Table 2.1. However, for the purpose of this study only physical (pH and EC) and hydrochemical (major ions) parameters are taken into consideration, and this is due to the fact that most of these major ions are directly involved in the hydrogeological and biochemical processes in a landfill environment.

Table 2.1 Leachate composition at various landfill sites in Malaysia (Samuding, 2010).

	Gemencheh, Negeri Sembilan	**Air Hitam, Puchong**	**Taman Beringin, Kuala Lumpur**
pH	5.0 – 5.6	7.6 – 8.8	7.9 – 8.8
Conductivity (μS/cm)	2290 – 2650	8640 – 33500	8800 – 35400
COD (mg/L)	NA	1724 – 7038	1960 – 5500
BOD (mg/L)	NA	1120 – 1800	562 – 1990
Na^+ (mg/L)	147 – 164	1530 – 5640	2616 – 5660
K^+ (mg/L)	266 – 316	719 – 1818	402 – 1940
Ca^{2+} (mg/L)	126 – 143	47 – 177	28 – 376
Mg^{2+} (mg/L)	21 – 30	41 – 105	31 – 109
SO_4^{2-} (mg/L)	106 – 115	18.5 – 110	40 – 79
Cl^- (mg/L)	322 – 357	1625 – 3200	875 – 2875
Ferum (mg/L)	0.1 – 1.5	3.6 – 15.7	3.2 – 17.42
Mangan (mg/L)	0.3 – 0.5	NA	NA
Nickel (mg/L)	0 – 0.10	0.13 – 0.95	0 – 0.60
Lead (mg/L)	0.02 – 0.03	0 – 5.37	0 – 3.45
Zinc (mg/L)	0.1 – 0.5	1.0 – 5.4	1.0 – 4.7
Cadmium (mg/L)	0 – 0.01	0 – 0.23	0 – 0.15
Chromium (mg/L)	0.04 – 0.28	0.24 – 0.94	0.04 – 0.70
Copper (mg/L)	0 – 0.1	0.05 – 0.49	0.15 – 0.46

NA=Not available.

2.2 Investigation on Leachate Movement and Impact

Under normal conditions, leachates are found at the bottom of landfills. It moves through the underlying strata, although some lateral movement may occur, depending on the characteristics of the surrounding material. As the leachate percolates, many of the original chemical and biological constituents contained within it will be removed

via filtering and adsorptive action of the material comprising the strata. Generally, the extent of this action largely depends on soil characteristics, especially its clay content (Peavy et al., 1985).

Literature results showed that under certain hydrologic conditions, leachate plume are capable of moving laterally at significant distances while degrading groundwater throughout wide areas. Exler (1974) described a situation in southern Bavaria, Germany, where the leachate plume migrated for more than 3000 meters from a landfill site. In Borden, Canada, Mac Farlane et al. (1983) disovered that the leachate plumes from the waste disposal site had migrated for up to 700 meters.

One of the main environmental concerns regarding landfilling is the phenomenon of leaching of contaminants, and the transport of these contaminants from the landfill into surface water and groundwater. In light of this fact, it is therefore crucial for a leachate to be contained within the landfill or removed altogether for treatment. An intricate understanding leachate movement is essential for long–term assessment of public safety and the protection of water resources. It is therefore logical to assume that the identification of leachate contamination will be of big help in the next step of leachate containment and its treatment process.

Leachate contamination investigation in water bodies are usually conducted using conventional method, measuring parameters such as pH, temperature, electrical conductivity (EC), dissolved oxygen (DO), major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-), heavy metals (Cadmium, zinc, lead, chromium, nickel and copper) and biological parameters (COD, BOD_5 and coliform group bacteria) in order

to evaluate the level of pollution. The interpretation of these data utilizes many techniques, the most prominent being the Piper Diagram (Figure 2.1). There are various references with regards to the application of this conventional method in order to study the impact of landfill leachate to surface water and groundwater (Tatsi and Zouboulis, 2002; Chofqi et al., 2004; Rapti–Caputo and Vaccaro, 2006; Al Sabahi et al., 2009). A similar approach was taken by Mohamed et al. (2009), based in Malaysia.

Although a large number of conventional methods exist for the study of leachate contamination in surface water and groundwater, these methods are not always successful in addressing all aspects of the systems. Meanwhile, environmental isotope techniques have proven effective in solving many critical hydrological problems. Taking into account these factors, the combination of the environmental isotope techniques with conventional hydrogeology and geochemistry techniques would be more conclusive.

2.2.1 Piper Diagram

The results from a hydrochemical analysis can be used to plot a Piper diagram (Figure 2.1) using a software called AQUACHEM. The piper diagram consists of three (3) triangles divided into different quadrants. The quadrant where the plot of the sample falls in is classified according to the stated ion groups (Leong, 2010). A piper diagram shows the concentrations in percentages, while also revealing similarities and differences among water samples, due to the fact that samples with similar qualities tend to be plotted together as groups (Todd, 1980). The mixture of two different water

samples will be plotted on a straight line that connects the two points (Freeze and Cherry, 1979).

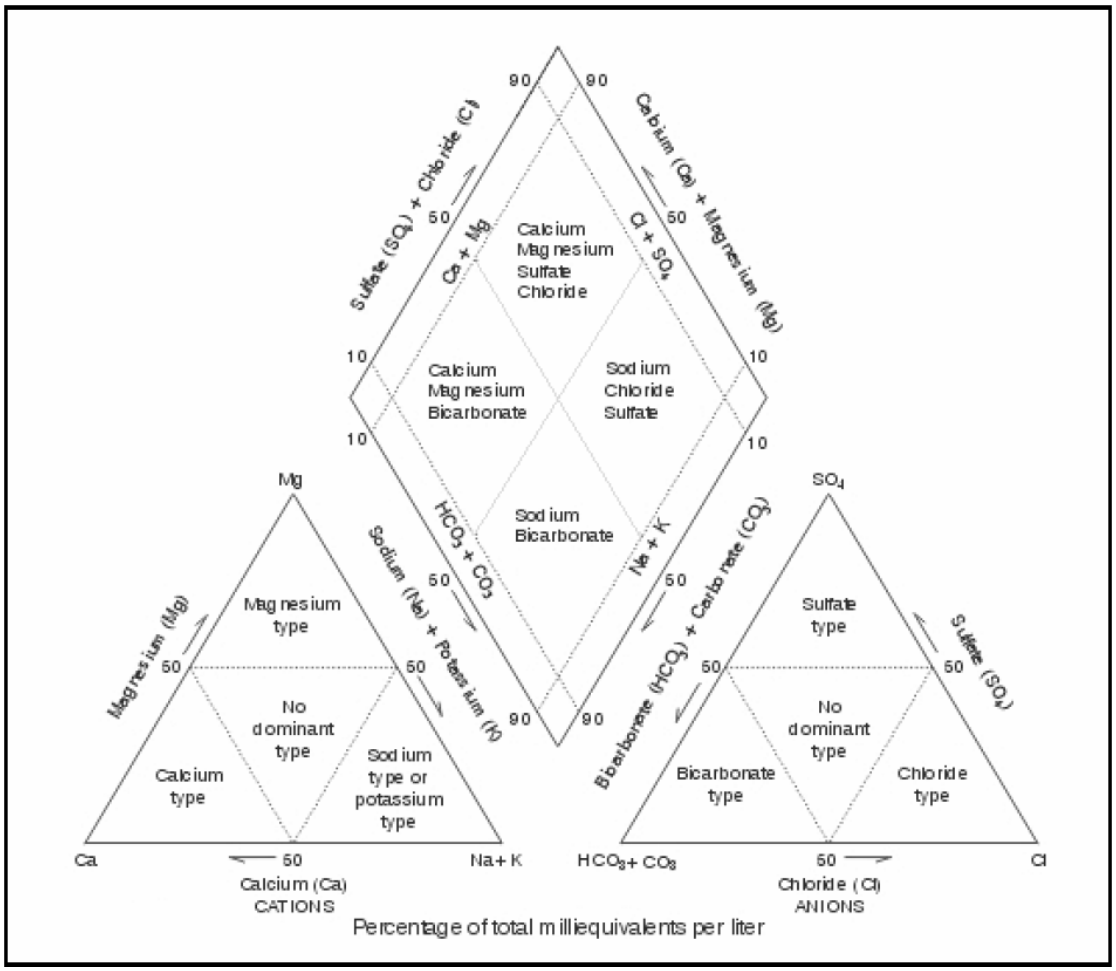

Figure 2.1 Guide for Piper diagram (Leong, 2010).

2.3 Fundamentals of Isotope Hydrology

The environmental isotopes technique is a useful tool in understanding the biogeochemical processes in the environment. The application of environmental isotopes acting as a hydrologic tracer can be divided into two main modes (i) a tracer for the water itself (*water isotope hydrology*) or (ii) a tracer for the solutes in the water (*solute isotope biogeochemistry*). Water isotope hydrology addresses the

application of isotopes that form water molecules such as oxygen (most common are ^{16}O and ^{18}O) and hydrogen isotopes (^{1}H, ^{2}H and ^{3}H), whereas solute isotope biogeochemistry addresses the application of isotopes of constituents that are dissolved in the water (Kendall and Caldwell, 1998), such as ^{13}C, ^{15}N and ^{34}S. The presence and detection of these constituents can provide valuable insights into reactions involving these elements in the environmental systems, thus serving as pollution tracers. Many hydrogeological studies use the environmental isotopes of water molecules to determine groundwater quality, its age and origin, its recharge mechanism, the water–rock interaction and its movement, transit times, and the source and mechanism of groundwater contamination (Kendall and Caldwell, 1998; Shivanna et al., 2008).

Isotopes are defined as atoms that have similar atomic number with different mass numbers; where atomic number is the total number of protons in a nucleus of an atom, while the mass number is the total number of neutrons *and* protons that are present in a nucleus. The element Hydrogen (H) demonstrates this phenomenon perfectly, where protium (H) or hydrogen, has a proton with no neutrons; deuterium (denoted as D or ^{2}H), has a proton and a neutron, while tritium (^{3}H) has a proton with two neutrons, making hydrogen and element with three isotopes (Chang, 1994).

Stable isotope compositions are generally reported as δ (pronounced delta) values in units of parts per thousand (denoted as ‰ or per mill), relative to a standard of known composition (e.g. Standard Mean Ocean Water, SMOW for $\delta^{2}H$ and $\delta^{18}O$; and Vienna Pee Dee Belemnite, VPDB for $\delta^{13}C$). The δ values are calculated using by Equation 1, in this case, for deuterium:

$$\delta^2H \text{ (in ‰)} = \frac{R_{Sample} - R_{Standard}}{R_{Standard}} \times 1000 \quad (1)$$

where R represents the ratio of heavy to light isotope ($^2H/^1H$), and R_{Sample} and $R_{Standard}$ are the isotope ratios in the sample and the standard respectively. The sample is called depleted (more negative) if the δ values are lower, and enriched (more positive) if the δ values are higher with respect to a reference (IAEA, 1983).

2.3.1 Stable Isotope Fractionation

The partitioning of isotopes between two substances or two phases of the same substance with different isotope ratios is called isotope fractionation (Hoefs, 2004). As a result of the fractionation processes, waters and solutes often develop a unique isotopic composition, which may be an indication of their sources or the processes that formed them. Two main types of phenomena, which produce isotope fractionation, are isotope exchange reactions and kinetic processes.

2.3.1.1 Isotope Exchange Reactions

Isotope exchange reactions or equilibrium fractionations involves the redistribution of isotopes between different chemical substances, different phases, or individual molecules in a closed, well–mixed system at chemical equilibrium. At isotopic equilibrium, the forward and backward reaction rates of any particular isotope are identical, meaning the ratio of the different isotopes in each compound remains constant for a particular temperature (Kendall and Caldwell, 1998; Mook, 2000a).

2.3.1.2 Kinetic Processes

Kinetic processes or kinetic fractionations are associated with incomplete and unidirectional chemical, physical and biological processes such as evaporation, dissociation reactions, biologically mediated reactions and diffusion. In a system not in chemical and isotopic equilibrium, forward and backward reaction rates are not identical and isotope reactions may be unidirectional only if reaction products are physically isolated from the reactants (Kendall and Caldwell, 1998; Mook, 2000a).

2.4 Stable Isotopes Application in Surface and Groundwater Studies

The conventional method of investigating surface water and groundwater contamination is by hydrochemical characterisation of water samples, where it is measured for major ions and heavy metals. However, the conventional method is limited in its capability to distinguish sources of pollution. This paves the way for the application of stable isotope techniques using ^{2}H, ^{18}O and ^{13}C, in detecting surface water and groundwater contamination. For example, in an estuarine environment (affected by sea water), the chloride level can be as high as 2500 mg/l (Libes, 1992). This reading has the potential to confuse the use of this parameter, for example in the identification of leachate contamination in surface waters and groundwater, as leachates in that environment was found to have chloride levels in the range of 1090–2732 mg/l (Mangimbulude et al., 2009).

Although numerous studies involving environmental isotopes in hydrogeology and geochemical investigations of the environment are available in the literature, there have been only a few applications of environmental isotopes in landfill studies.

Environmental isotopes generally refer to the naturally occurring isotopes of hydrogen (^{1}H, ^{2}H, and ^{3}H), carbon (^{12}C, ^{13}C, and ^{14}C), nitrogen (^{14}N and ^{15}N), oxygen (^{16}O and ^{18}O) and sulphur (^{32}S and ^{34}S). Several studies were conducted using stable isotopes of ^{2}H, ^{13}C and ^{18}O to measure the $\delta^{2}H$, $\delta^{13}C$ and $\delta^{18}O$ values in a landfill leachate. A study conducted by Abdul Rahman et al. (2006) at the same landfill site shows that the $\delta^{2}H$–water and $\delta^{18}O$–water values for leachate range from –28.8‰ to –9.9‰ and –1.9‰ to –4.5‰ respectively, while the $\delta^{2}H$–water and $\delta^{13}C$–DIC isotopic values range from –47‰ to –4‰ and 2.8‰ to 15.8‰ respectively, and was obtained from the landfill leachate of four diverse landfill sites in New Zealand (North et al., 2006). The results of $\delta^{2}H$–water for surface water (river) in both the studies ranged from –48.6‰ to –28.8‰ (Abdul Rahman et al., 2006) and –62.0‰ to –22.3‰ (North et al., 2006). The characteristics of ^{2}H (deuterium), ^{13}C and ^{18}O are described for landfill leachate, surface water and groundwater. However, sulphur and nitrogen isotopes were not examined, since their concentrations in the leachate are usually very low (Hackley et al., 1996). $\delta^{2}H$–water for leachate was found having more enriched (more positive) values compared to surface water (river). Therefore, the different values of the leachate can be used as a guide or reference in landfill leachate contamination studies.

In The Netherlands, van Breukelen et al. (2003) conducted a study to determine the redox processes in a landfill leachate plume in groundwater using various

methodologies such as the distribution of solid and soluble redox species, hydrogen concentrations, and the concentration of dissolved gases and stable isotopes (including δ^{13}C–DIC). The δ^{13}C–DIC in the plume decreases in the downstream direction from 13.1‰ at the landfill border to 9.6‰ further downstream, and these values are strongly enriched compared to the background, –19.6‰ (pristine groundwater). Atekwana and Krishnamurthy (2004) investigated the impact of landfill-contaminated groundwater along a small stream, adjacent to a municipal landfill in Michigan, USA, using stable carbon isotopes (^{13}C) as a tracer. Groundwater samples, seeping into the stream were collected using a specifically designed device called a 'seepage well'. The δ^{13}C–DIC isotopic ratios of the adjacent stream bank groundwater, groundwater below the stream and groundwater seepage into the stream are enriched (–2.3‰ to 5.7‰), compared to the stream bank opposite the landfill (–10.0‰ to –16.9‰). Bacterially mediated methanogenesis in municipal solid waste landfills has been shown to cause enrichment of carbon stable isotope ratios of dissolved inorganic carbon (and also hydrogen stable isotope ratios) of water in landfill leachate (North et al., 2006). Arneth (1988), cited by North et al. (2004), identified an unusually high δ^{13}C–DIC value in groundwater wells suspected of leachate contamination. However, the enrichment of carbon stable isotope ratios in water could also result from the mixing process between landfill leachate–polluted water and uncontaminated water. This happens as the leachate flows downstream, forming the leachate plume.

North et al. (2004) suggested the potential application of ^{13}C and ^{15}N isotopic characteristics as a tool to monitor the impact of landfills to their surrounding environment. The average results of isotopic analysis for δ^{13}C of DIC component for

the leachate, upstream and downstream were 16.11‰, –15.09‰ and 20.18‰, respectively. The downstream site, with an enriched value, are most likely caused by the leachate entering the stream at some point below the upstream sampling area, as the leachate samples clearly exhibited significantly enriched δ^{13}C–DIC values. Again, North et al. (2006) used stable isotopes to detect leachate contamination in landfill–associated streams. Surface water samples, upstream and downstream from four landfill sites were analysed for carbon stable isotope ratios of dissolved inorganic carbon (δ^{13}C–DIC) and hydrogen stable isotope ratios of water (δ^{2}H–water). Two of the sites were found to have a depleted δ^{13}C–DIC value, and one with indistinguishable isotope ratios compared to the upstream. As for δ^{2}H–water results, three of the sites showed no significant difference between upstream and downstream. Therefore, confounding factors such as upstream contaminant sources, leachate dilution by water source systems and comprehensive knowledge of each site (such as geologic conditions, among others) should be taken into consideration during the interpretation of the isotopic results. The absence of measurable landfill leachate with contaminated surface water downstream may be the result of a higher volume of stream flow, relative to the leachate seeping into the river.

According to Hackley et al. (1996) and North et al. (2006), the stable isotope characteristics of leachate–associated aqueous media are quite unique in the landfill surrounding environments, due to the biologically mediated methanogenic processes associated with refuse decomposition. These processes result in the isotopic enrichment of carbon in dissolved inorganic carbon (δ^{13}C–DIC), hydrogen (δ^{2}H) and oxygen (δ^{18}O) isotopes of water in landfill leachate. The enrichment of leachate δ^{13}C–

DIC is caused by methane–producing bacteria, preferring to use the lighter ^{12}C to form CH_4 (Whiticar et al., 1986; Grossman et al., 2002).

Chofqi et al. (2004) carried out a study to evaluate the impact of an urban landfill on groundwater pollution. In Morocco, uncontrolled dumping sites with no bottom liner was found to have high values of EC (more than 4500μS/cm), chloride (1600mg/L), and other organic and inorganic chemicals in the groundwater, in the vicinity of the landfill. The main pollution source is linked to the infiltration of a leachate, which conveys a strong pollutant load, and direct contact of the leachate with waters of the aquifer in the landfill. The authors also recommended the usage of isotopic tracers for future studies in order to better gain a comprehensive understanding of groundwater dynamics.

On top of investigating sources and the mechanism of water bodies contamination, ^{2}H and ^{18}O isotopes can also be used to study the movements, the source and mechanism of recharge, and the transit times of surface water and groundwater. Wilcox et al. (2004) performed a study using stable isotopes of ^{2}H and ^{18}O to quantify the flows in surface water and groundwater in a study area, covering a protected wetland environment at Everglades National Park and a Miami suburban residential area in Florida. The study clearly indicates the movement of surface waters including lakes, shallow and deep groundwater of the aquifer, and also quantified the amount of water being drawn into the operating municipal pumping wells originating from the Everglades (60%). Lee et al. (2007) analysed the water movement through an unsaturated soil zone in Jeju Island, Korea using stable isotopes of ^{2}H and ^{18}O. From the study, the stable ^{2}H and ^{18}O isotopic compositions indicated that the soil waters

were recharged from the year–round precipitation. The mean residence times (MRT) of the soil waters from the δ^2H, $\delta^{18}O$ and deuterium excess or *d*–values using statistical models were also estimated. MRT for soil waters at the depth of 30cm and 60cm range from 52.0 – 78.6 days and 53.9 – 377.2 days, respectively. Surface water contributions (recharge) in the groundwater can be a source of quality reduction in drinking water wells as groundwater is vulnerable to contaminants present in surface water. Hunt et al. (2005) utilized the stable hydrogen and oxygen isotope ratios of water to determine the contribution and traveling time of surface water in groundwater in Wisconsin, USA. The estimated time of travel from river to groundwater (municipal wells) were 2 months for flood conditions and 9 months for non–flood conditions. This successfully concluded the use of hydrogen and oxygen stable isotopes as an effective tool for describing the influence of surface water on municipal well supplies. The use of δ^2H and $\delta^{18}O$ demonstrates the ability to articulate the understanding of water movement in the water systems. This also proves that δ^2H and $\delta^{18}O$ are better tracers for evaluating the recharge process. In addition to identifying the source of water, the analyses of stable hydrogen and oxygen isotope ratios of water over time can provide valuable insight into the time of travel from a surface water source to the well.

Stable isotope of ^{13}C and ^{15}N were also used in groundwater and surface water studies other than ^2H and ^{18}O. Chen et al. (2005) used the stable isotopes of ^2H, ^{18}O and ^{15}N to identify nitrate contamination of groundwater in a wastewater irrigated field near the city of Shijiazhuang, China. $\delta^{15}N$ was earlier found in a range of 10–22‰ for the source of manure/urine and 2–9‰ for natural soil organic–N (Kreitler and Jones, 1975; Heaton, 1986; Clark and Fritz, 1997). The $\delta^{15}N$–nitrate values in the

groundwater samples in the study area were between 7 and 11‰ AIR (referred to atmospheric N_2 standard), and this indicates that the nitrate come is a result of a mixture of those two sources. Therefore, the nitrogen isotopic composition results confirm that the nitrate present in contaminated groundwater originates from the wastewater.

2.4.1 Fractionation of ^{13}C by Methanogenesis Process in Water

According to Hackley et al. (1996), during methanogenesis, the enrichment of leachate $\delta^{13}C$–DIC is caused by a methane–producing bacteria, preferring to use the lighter ^{12}C to form CH_4, which resulted in a CH_4 that is enriched with lighter carbon isotope (^{12}C), with the CO_2 associated with microbial methane production is enriched in the heavier carbon isotope (^{13}C), as detailed in Equation 2 (Clark and Fritz, 1997):

$$2CH_2O \text{ (organic matter)} \leftrightarrow CO_2 + CH_4 \qquad (2)$$

The concurrent shift in $\delta^{13}C$ is large, but rather uncertain, as there is a strong but variable kinetic isotope fractionation involved. Usually the CO_2 becomes isotopically enriched in ^{13}C, which qualitatively allows for the identification of the process (Mook, 2000b).

This heavier isotope of ^{13}C–enriched–CO_2 contributed to the Dissolved Inorganic Carbon (DIC) in waters, as DIC is known as the sum of inorganic carbon species which are; dissolved CO_2, carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). Although DIC is dominated by HCO_3^-, dissolved CO_2 is present in

comparable quantity (van Breukelen et al., 2003), with each species intimately related to pH driven chemical equilibria, as represented by Equation 3 (Mook, 2000a).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \quad (3)$$

This clarifies why the leachate–impacted water samples were found to contain a distinct isotopic signature, characterised by a highly enriched $\delta^{13}C$–DIC values. This also applies to other isotopes, as ^{2}H and ^{18}O will get noticeably enriched during the methanogenesis process.

If livestock or ruminant effluent were a significant nutrient/contamination source in the rivers, then a lighter or depleted $\delta^{13}C$–DIC value would be expected rather than the enriched value as the $\delta^{13}C$ value for the ruminant effluent would be expected to reflect that of the animals' diet (Wahlen, 1994), which are typically plants, with a reported $\delta^{13}C$ value in the range of –22‰ to –27‰ (Lajtha and Marshall, 1994).

2.5 Previous Work on Surface and Groundwater Studies Using Stable Isotopes in Malaysia

Currently, no research is being undertaken to study the landfill leachate contamination using stable isotopes of ^{13}C in Malaysia. Abdul Rahman et al. (2006) used stable isotopes of ^{2}H and ^{18}O to study the interconnection between leachate–groundwater–surface waters and tritium to determine the age (the water is mixed of sub–modern and modern groundwater) of the water samples at the same landfill site. This might be due to the absence of IRMS instrument in Malaysia, as it is very expensive and only

available at Malaysian Nuclear Agency since 2008. Another reason might also be the lack of experience and knowledge on the sample preparation methods for IRMS analysis.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

This research project was designed to determine whether the isotopic ratio of $\delta^{2}H$, $\delta^{13}C$ and $\delta^{18}O$ could be used to distinctly identify municipal solid waste landfill leachate as a source of surface waters and groundwater contamination in the study area. In this project, surface water samples from upstream and downstream of landfill related rivers, ponds, and groundwater samples within the landfill site, together with the leachate samples, were analysed to study the applicability of the stable isotope ratios as a tool for monitoring leachate contamination in surface waters and groundwater. All the water samples were measured for $\delta^{2}H$–water, $\delta^{18}O$–water and $\delta^{13}C$–DIC (Dissolved Inorganic Carbon) values. The values of the stable isotopes obtained from surface waters and groundwater samples were studied and compared with the leachate to decisively fingerprint the possibility of contamination. The application of nuclear related technology in this study was carried out using Isotope Ratio Mass Spectrometer (IRMS) to analyse all the water samples for isotopic ratio.

3.2 Site Description

The landfill site covers a 20–hectare area (Figure 3.1). The landfilling operations started in 1995 and since then, over 1,000,000 metric tonnes (approximately 75,000 tonnes annually) of domestic wastes have been dumped in the landfill. The site is an